

## 1. PROJECT OVERVIEW

### Test Program Summary

Air Products and Chemicals, Inc. (Air Products) contracted CleanAir Engineering (CleanAir) to successfully complete emissions compliance measurements at the Detroit Hydrogen Plant. The testing was performed at the Hydrogen (H<sub>2</sub>) Plant Heater Stack. The test program included the following objectives:

- To perform a relative accuracy test audit (RATA) on the continuous emission monitoring system (CEMS);
- To determine compliance for particulate matter (PM) and PM<sub>10</sub>;
- To determine emissions of sulfuric acid mist (H<sub>2</sub>SO<sub>4</sub>);
- To determine compliance for volatile organic compounds (VOCs).

A summary of the test program results is presented below. Section 2 Results provides a more detailed account of the test conditions and data analysis. Test program information, including the test parameters, on-site schedule and a project discussion, begins on page 2.

**Table 1-1:  
Summary of Emissions Compliance Test Results**

Source	Constituent (Units)	Sampling Method	Average Emission	Permit Limit <sup>†</sup>
H <sub>2</sub> Plant Heater Stack				
PM	(lb/MMBtu)	USEPA M-5	0.00063	0.0034
PM	(Ton/yr)	USEPA M-5	1.72	6.86
PM <sub>10</sub>	(lb/MMBtu)	USEPA M-5 / 202	0.0025	0.010
H <sub>2</sub> SO <sub>4</sub>	(lb/MMBtu)	Modified CTM-013	0.000069	N/A
VOC	(lb/MMBtu)	USEPA M-25A/18	<0.00065	0.0055
NO <sub>x</sub>	(lb/MMBtu)	USEPA M-7E	0.0084	0.013
NO <sub>x</sub>	(ppm dv @ 0% O <sub>2</sub> )	USEPA M-7E	7.8	60
CO	(Ton/yr)	USEPA M-10	< 1.1	13

<sup>†</sup> Permit limits obtained from MDEQ Permit to Install No. 63-08D.

**Table 1-2:  
Summary of RATA Results**

Source Constituent (Units)	Reference Method (USEPA)	Relative Accuracy <sup>1</sup>	Units	Applicable Specification	Specification Limit <sup>2</sup>
H <sub>2</sub> Plant Heater Stack					
Flow rate (dscfh)	M-2	9.3	% of RM	PS6	20% of RM
O <sub>2</sub> (% dv)	M-3A	0.07	%dv	PS3	± 1.0% dv
H <sub>2</sub> O (% ww)	M-4	19.2	% of RM	N/A	N/A
NO <sub>x</sub> (ppmdv)	M-7E	11.6	% of RM	PS2	20% of RM
NO <sub>x</sub> (lb/MMBtu)	M-7E	13.4	% of RM	PS2	20% of RM
NO <sub>x</sub> (ppmdv @ 0%O <sub>2</sub> )	M-7E	12.3	% of RM	PS2	20% of RM
CO (ppmdv)	M-10	0.50	ppmdv	PS4A <sup>3</sup>	± 5 ppmdv
CO (lb/hr)	M-10	0.45	% of Std.	PS4A <sup>3</sup>	5% of Standard <sup>4</sup>

<sup>1</sup> Relative Accuracy is expressed in terms of comparison to the reference method (% RM) or applicable emission standard (% Std.), equivalent to the permit limit in Table 1-2. The specific expression used depends on the specification limit.

<sup>2</sup> Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications, unless otherwise noted.

<sup>3</sup> For any sources emitting less than 200 ppmv of CO, PS4A applies. The PS4ARA limit is either < 10% of RM, <5% of Standard, or ± 5 ppmv (abs. average difference plus 2.5 x confidence coefficient).

<sup>4</sup> CO Standard = 13 Ton/yr = 56.9 lb/hr (assuming 8,760 operating hours/year)

## Test Program Details

### Parameters

The test program included the following measurements:

- PM assumed equivalent to filterable particulate matter (FPM)
- condensable particulate matter (CPM)
- particulate matter less than 10 microns in diameter (PM<sub>10</sub>) assumed to be the sum of:
  - FPM
  - CPM
- Sulfuric acid mist (H<sub>2</sub>SO<sub>4</sub>)
- VOCs assumed equivalent to total hydrocarbons (THCs) minus:
  - methane (CH<sub>4</sub>)
  - ethane (C<sub>2</sub>H<sub>6</sub>)
- nitrogen oxide (NO<sub>x</sub>)
- carbon monoxide (CO)
- flue gas composition (e.g., O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O)
- flue gas temperature
- flue gas flow rate

## Schedule

Testing was performed on March 6 and 7, 2019. The on-site schedule followed during the test program is outlined in Table 1-3.

**Table 1-3:  
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	H2 Heater Stack	USEPA Method 5/202	FPM/CPM	03/06/19	9:50	12:19
1	H2 Heater Stack	USEPA Method 3A, 25A	O <sub>2</sub> /CO <sub>2</sub> , VOC	03/06/19	11:52	12:52
2	H2 Heater Stack	USEPA Method 5/202	FPM/CPM	03/06/19	12:48	15:00
2	H2 Heater Stack	USEPA Method 3A, 25A	O <sub>2</sub> /CO <sub>2</sub> , VOC	03/06/19	13:17	14:17
3	H2 Heater Stack	USEPA Method 5/202	FPM/CPM	03/06/19	15:34	17:59
3	H2 Heater Stack	USEPA Method 3A, 25A	O <sub>2</sub> /CO <sub>2</sub> , VOC	03/06/19	15:41	16:41
1	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	09:55	10:16
1	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	09:59	10:07
1	H2 Heater Stack	Modified CTM-013	H <sub>2</sub> SO <sub>4</sub> / Moisture	03/07/19	10:06	11:16
2	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	10:37	10:58
2	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	10:48	10:54
3	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	11:20	11:25
3	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	11:20	11:41
4	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	11:58	12:19
2	H2 Heater Stack	Modified CTM-013	H <sub>2</sub> SO <sub>4</sub> / Moisture	03/07/19	12:11	13:21
4	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	12:12	12:21
5	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	12:44	13:05
5	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	12:45	12:51
6	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	13:41	14:02
6	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	13:43	13:49
7	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	14:35	14:41
7	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	14:35	14:56
3	H2 Heater Stack	Modified CTM-013	H <sub>2</sub> SO <sub>4</sub> / Moisture	03/07/19	14:55	16:05
8	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	15:16	15:22
8	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	15:16	15:37
9	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	15:57	16:03
9	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	15:57	16:18
10	H2 Heater Stack	USEPA Method 2	Velocity & Flow Rate	03/07/19	16:45	16:51
10	H2 Heater Stack	USEPA Method 3A, 7E, 10	O <sub>2</sub> /CO <sub>2</sub> , NO <sub>x</sub> , CO	03/07/19	16:39	17:00
4	H2 Heater Stack	USEPA Method 4	Moisture	03/07/19	16:44	17:19

## Discussion

### *Project Synopsis*

CleanAir conducted the sample program over a two-day span. During the first test day, three (3) EPA Method 5/202 test runs were conducted along with three (3) EPA Method 25A test runs.

The RATA was conducted during the second test day, along with EPA Method 2 traverses for flow measurements and three (3) modified Conditional Test Method 013 (CTM-013) test runs for sulfuric acid ( $H_2SO_4$ ) mist. The CTM-013 test runs were used for moisture determination for the coinciding flow measurement calculations. In addition, one (1) EPA Method 4 test run for moisture was conducted to coincide with the final flow measurement (Run 10).

The plant had several invalid data points during Run 5; therefore, that run was excluded from all RATA calculations.

A cyclonic flow check, per EPA Method 1 Section 11.4, was performed prior to any test runs being performed. The sampling location met method criteria. The cyclonic flow check data sheet is presented in Appendix E of this report.

### USEPA Method 5/202

For this test program, the PM emission rate is assumed equivalent to the FPM emission rate. The  $PM_{10}$  emission rate is assumed equivalent to the sum of FPM and CPM emission rates (units of lb/hr, Ton/yr, or lb/MMBtu for all constituents).

The analytical procedures in Method 202 include an ammonium titration of the inorganic sample fractions with pH less than 7.0 to neutralize acids with hygroscopic properties (such as  $H_2SO_4$ ) that may be present in the sample. This step speeds up the sample desiccation process and allows the samples to come to a constant weight prior to weighing. The weight of ammonium added to the sample as a result of the titration is subtracted from the analytical result.

CleanAir Analytical Services in Palatine, Illinois, performed the gravimetric analysis and determined that only samples with an initial pH less than 4.5 require a significant amount of ammonium neutralization, resulting in a correction in excess of 0.5 mg. Based on this observation, the laboratory has altered its procedures to read that a sample must have a pH lower than 4.5 in order to be titrated.

The final results for each parameter were expressed as the average of three runs and were below the permit limits for both PM and  $PM_{10}$ .

### Modified Conditional Test Method 13

Three test runs were performed on March 7. The final result was expressed as the average of three valid runs (Runs 1, 2 and 3).

### USEPA Method 25A

Three valid Method 25A test runs for THCs were performed concurrently with the three (3) Method 5/202 test runs on March 6. The final results for each parameter were expressed as the average of three valid runs (Runs 1, 2 and 3).

Method 25A states that the mid-range calibration gas should be used for the drift checks between runs. Because the flue gas contained very low levels of hydrocarbons, the operator used the low-level calibration gas for the drift checks.

VOC emission rate is normally equivalent to THC emission rate, minus CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> emission rate (units of lb/hr, Ton/yr or lb/MMBtu for all constituents). For all runs, the THC concentration was below the reportable instrument response (considered to be 1% of instrument span, 0.45 ppm, vw); therefore, no Method 18 sample bags were collected, and no CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> correction were made.

### USEPA Methods 2, 3A, 4, 7E, and 10 – Performance Specifications 2, 3, 4A, and 6

#### Sample Approach

One-minute average data points for O<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub> and CO (dry basis) were collected over a period of 21 minutes for each RATA reference method (RM) run.

The average result for each RM run was calculated and compared to the average result from the facility CEMS over identical time intervals in order to calculate relative accuracy (RA):

- For O<sub>2</sub> (%dv), RA is expressed as the average absolute difference between the RM and facility CEMS runs. The final result was below the limit of  $\pm 1.0\%$  dv set by Performance Specification (PS) 3.
- For NO<sub>x</sub> (ppmdv) concentration, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 20% of the RM set by PS 2.
- For NO<sub>x</sub> (lb/MMBtu) emission rate, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 20% of the RM set by PS 2.
- For NO<sub>x</sub> (ppmdv @ 0% O<sub>2</sub>) concentration, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 20% of the RM set by PS 2.
- For CO (ppmdv) concentration, the RA limit is expressed as the average absolute difference between the RM and facility CEMS runs, plus 2.5 times the confidence coefficient. The final result was below the limit of  $\pm 5$  ppmdv set by PS 4A, which is applicable to sources that emit less than 200 ppmv of CO.
- For CO (lb/hr) diluent, RA is expressed as the percent difference between RM and facility CEMS runs. The final result was below the limit of 5% of the standard (permit limit listed in Table 1-2 on page 2) set by PS 4A.
- CO<sub>2</sub> data was collected only as supplemental information.
- Moisture data presented in Table 2-8 on page 15 is for comparison purposes only.

All CO concentrations measured were below the instrument reportable response (considered to be 1% of instrument span, 0.479 ppm, dv).

Facility flow rate CEMS were evaluated using Method 2 as the RM. A complete flow and temperature traverse was performed during each 21-minute RATA run, converted to units of dry standard cubic feet per hour (dscfh), and then compared to the facility CEMS results over the corresponding 21-minute intervals.

The flow rate, RA, is expressed as the percent difference between RM and facility CEMS data. The final results were below the limit of 20% of the RM set by PS 6.

Moisture data was used to convert flow rate from wet basis to dry basis and was obtained from concurrently operated CTM-013 test runs:

- For RATA Runs 1, 2, and 3, H<sub>2</sub>O data was obtained from CTM-013 Run 1.
- For RATA Runs 4, 5, and 6, H<sub>2</sub>O data was obtained from CTM-013 Run 2.
- For RATA Runs 7, 8, and 9, H<sub>2</sub>O data was obtained from CTM-013 Run 3.
- For RATA Run 10, H<sub>2</sub>O data was obtained from a single Method 4 test run.

NO<sub>x</sub> and CO results from the RATA were converted from units of dry volume-based concentration (ppmdv) to mass-based emission rate units (lb/hr, Ton/yr, and lb/MMBtu) to demonstrate compliance with permit limits. The final results for each parameter were expressed as the average of nine (9) RATA runs. The final results were below the permit limits.

### Calculation of Final Results

Emission results in units of dry volume-based concentration (lb/dscf, ppmdv) were converted to units of lb/MMBtu using the F<sub>d</sub> factor method. Fuel F<sub>d</sub> factors were provided by Air Products. Flow rates used in calculating lb/hr emissions were obtained in the following manner:

- For Method 5/202, flow rate measurements are incorporated into the sampling procedures.
- For Method 25A, flow rate measurements from the most nearly concurrent Method 5/202 test runs were used.
- For Method 7E/10, a flow rate measurement, per Method 2 specifications, was performed concurrently with each test run.
- For CTM-013, the flow rate measurements made concurrently with the Method 7E/10 run that most closely corresponded were used.

### General Considerations

All run times listed throughout this report correspond to the plant time utilized by Air Products. Plant time is the time of the Air Products CEMS and data acquisition system.

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*End of Section*

## 2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices, specifically Appendix C Parameters.

**Table 2-1:  
H<sub>2</sub>SO<sub>4</sub> Emissions**

Run No.	1	2	3	Average
Date (2019)	Mar 7	Mar 7	Mar 7	
Start Time (approx.)	10:06	12:11	14:55	
Stop Time (approx.)	11:16	13:21	16:05	
<b>Process Conditions</b>				
R <sub>p</sub> Hydrogen production rate (Mscf/day)	58.0	59.0	58.9	<b>58.6</b>
P <sub>1</sub> Aqueous NH <sub>3</sub> feed rate to SCR (lb/hr)	32.0	32.9	33.4	<b>32.8</b>
P <sub>2</sub> SCR Inlet temperature (°F)	624	629	630	<b>628</b>
F <sub>d</sub> Oxygen-based F-factor (dscf/MMBtu)	8,986	8,990	8,988	<b>8,988</b>
Cap Capacity factor (hours/year)	8,760	8,760	8,760	<b>8,760</b>
<b>Gas Conditions</b>				
O <sub>2</sub> Oxygen (dry volume %)	3.1	3.1	3.2	<b>3.1</b>
CO <sub>2</sub> Carbon dioxide (dry volume %)	18.7	18.6	18.5	<b>18.6</b>
T <sub>s</sub> Sample temperature (°F)	326	326	327	<b>326</b>
B <sub>w</sub> Actual water vapor in gas (% by volume)	14.3	15.2	12.8	<b>14.1</b>
<b>Gas Flow Rate</b>				
Q <sub>a</sub> Volumetric flow rate, actual (acfm)	202,000	204,000	201,000	<b>202,000</b>
Q <sub>s</sub> Volumetric flow rate, standard (scfm)	134,000	135,000	133,000	<b>134,000</b>
Q <sub>std</sub> Volumetric flow rate, dry standard (dscfm)	115,000	115,000	116,000	<b>115,000</b>
<b>Sampling Data</b>				
V <sub>mstd</sub> Volume metered, standard (dscf)	26.39	26.01	25.50	<b>25.97</b>
<b>Laboratory Data (Ion Chromatography)</b>				
m <sub>n</sub> Total H <sub>2</sub> SO <sub>4</sub> collected (mg)	0.0411	0.1142	0.0758	
<b>Sulfuric Acid Mist (H<sub>2</sub>SO<sub>4</sub>) Results</b>				
C <sub>sd</sub> H <sub>2</sub> SO <sub>4</sub> Concentration (lb/dscf)	3.4E-09	9.7E-09	6.6E-09	<b>6.6E-09</b>
C <sub>sd</sub> H <sub>2</sub> SO <sub>4</sub> Concentration (ppmdv)	0.013	0.038	0.026	<b>0.026</b>
E <sub>lb/hr</sub> H <sub>2</sub> SO <sub>4</sub> Rate (lb/hr)	0.024	0.067	0.046	<b>0.045</b>
E <sub>T/yr</sub> H <sub>2</sub> SO <sub>4</sub> Rate (Ton/yr)	0.104	0.29	0.20	<b>0.20</b>
E <sub>Fd</sub> H <sub>2</sub> SO <sub>4</sub> Rate - Fd-based (lb/MMBtu)	0.000036	0.000102	0.000070	<b>0.000069</b>

**Table 2-2:  
FPM, CPM and Total PM<sub>10</sub> Emissions (EPA Method 5/202)**

Run No.		1	2	3	Average
Date (2019)		Mar 6	Mar 6	Mar 6	
Start Time (approx.)		09:50	12:48	15:34	
Stop Time (approx.)		12:19	15:00	17:59	
<b>Process Conditions</b>					
R <sub>P</sub>	Hydrogen production rate (Mscf/day)	56.0	56.1	57.7	<b>56.6</b>
P <sub>1</sub>	Aqueous NH <sub>3</sub> feed rate to SCR (lb/hr)	30.4	30.6	32.4	<b>31.1</b>
P <sub>2</sub>	SCR Inlet temperature (°F)	617	617	625	<b>620</b>
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	9,004	9,004	9,008	<b>9,005</b>
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	3.2	3.2	3.3	<b>3.2</b>
CO <sub>2</sub>	Carbon dioxide (dry volume %)	18.5	18.5	19.9	<b>19.0</b>
T <sub>s</sub>	Sample temperature (°F)	324	324	325	<b>324</b>
B <sub>w</sub>	Actual water vapor in gas (% by volume)	15.0	14.7	14.4	<b>14.7</b>
<b>Gas Flow Rate</b>					
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	196,000	194,000	197,000	<b>196,000</b>
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	130,000	128,000	131,000	<b>130,000</b>
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	110,000	110,000	112,000	<b>111,000</b>
<b>Sampling Data</b>					
V <sub>mstd</sub>	Volume metered, standard (dscf)	76.92	76.03	78.49	<b>77.15</b>
%I	Isokinetic sampling (%)	99.5	99.0	100.2	<b>99.6</b>
<b>Laboratory Data</b>					
m <sub>n</sub>	Total FPM (g)	0.00241	0.00151	0.00231	
m <sub>CPM</sub>	Total CPM (g)	0.00619	0.00539	0.00673	
m <sub>Part</sub>	Total particulate matter (g)	0.00860	0.00690	0.00904	
<b>FPM Results</b>					
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	0.458	0.288	0.435	<b>0.394</b>
E <sub>T/yr</sub>	Particulate Rate (Ton/yr)	2.00	1.26	1.91	<b>1.72</b>
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.00073	0.00047	0.00069	<b>0.00063</b>
<b>CPM Results</b>					
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	1.18	1.03	1.27	<b>1.16</b>
E <sub>T/yr</sub>	Particulate Rate (Ton/yr)	5.15	4.51	5.56	<b>5.07</b>
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.0019	0.0017	0.0020	<b>0.0019</b>
<b>Total Particulate Matter Results</b>					
E <sub>lb/hr</sub>	Particulate Rate (lb/hr)	1.63	1.32	1.70	<b>1.55</b>
E <sub>T/yr</sub>	Particulate Rate (Ton/yr)	7.15	5.77	7.46	<b>6.80</b>
E <sub>Fd</sub>	Particulate Rate - F <sub>d</sub> -based (lb/MMBtu)	0.0026	0.0021	0.0027	<b>0.0025</b>



**Table 2-3:  
VOC Emissions (EPA Method 25A)**

Run No.		1	2	3	Average
Date (2019)		Mar 6	Mar 6	Mar 6	
Start Time (approx.)		11:52	13:17	15:11	
Stop Time (approx.)		12:52	14:17	16:12	
<b>Process Conditions</b>					
P <sub>1</sub>	Hydrogen Production (Mscf/day)	56.0	56.1	58.4	56.8
P <sub>2</sub>	Aqueous NH <sub>3</sub> feed to SCR (lb/hr)	30.3	30.6	32.7	31.2
P <sub>3</sub>	SCR Inlet Temperature	617	617	626	620
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	9,004	9,004	9,013	9,004
H <sub>i</sub>	Actual heat input (MMBtu/hr)	582	583	609	592
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760
<b>Gas Conditions</b>					
O <sub>2</sub>	Oxygen (dry volume %)	3.1	3.2	3.2	3.2
CO <sub>2</sub>	Carbon dioxide (dry volume %)	18.4	18.5	18.5	18.5
B <sub>w</sub>	Actual water vapor in gas (% by volume) <sup>1</sup>	15.5	15.5	15.7	15.5
<b>Gas Flow Rate<sup>2</sup></b>					
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	196,000	194,000	197,000	196,000
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	130,000	128,000	131,000	130,000
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	110,000	110,000	112,000	111,000
<b>THC Results (as Propane)<sup>3</sup></b>					
C <sub>sd</sub>	Concentration (ppmdv)	<0.53	<0.53	<0.53	<0.53
C <sub>sd</sub>	Concentration (lb/dscf)	<6.1E-08	<6.1E-08	<6.1E-08	<6.1E-08
E <sub>lb/hr</sub>	Emission Rate (lb/hr)	<0.40	<0.40	<0.41	<0.40
E <sub>T/yr</sub>	Emission Rate (Ton/yr)	<1.8	<1.8	<1.8	<1.8
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<0.00065	<0.00065	<0.00065	<0.00065
E <sub>Hi</sub>	Emission Rate - Heat input-based (lb/MMBtu)	<0.00069	<0.00069	<0.00067	<0.00068

<sup>1</sup> Moisture data used for ppmwv to ppmdv correction obtained from nearly-concurrent M-5/202 runs.<sup>2</sup> Flow data used in lb/hr calculations was obtained from nearly-concurrent Method 5/202 runs .<sup>3</sup> '<' indicates a measured response below the detection limit (assumed to be 1% of instrument span).

**Table 2-4:  
NO<sub>x</sub> and CO Emissions (EPA Method 7E/10)**

Run No.		1	2	3	4	5	6
Date (2019)		Mar 7	Mar 7	Mar 7	Mar 7	Mar 7	Mar 7
Start Time (approx.)		09:55	10:37	11:20	11:58	12:44	13:41
Stop Time (approx.)		10:16	10:58	11:41	12:19	13:05	14:02
<b>Process Conditions</b>							
P <sub>1</sub>	Hydrogen Production (Mscf/day)	58.7	58.7	58.7	58.7	58.7	58.7
P <sub>2</sub>	Aqueous NH <sub>3</sub> feed to SCR (lb/hr)	32.8	32.8	32.8	32.8	32.8	32.8
P <sub>3</sub>	SCR Inlet Temperature	628	628	628	628	628	628
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,986	8,987	8,986	8,992	8,990	8,990
H <sub>i</sub>	Actual heat input (MMBtu/hr)	602	602	602	602	602	602
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760	8,760	8,760
<b>Gas Conditions</b>							
O <sub>2</sub>	Oxygen (dry volume %)	3.1	3.1	3.1	3.1	3.1	3.1
CO <sub>2</sub>	Carbon dioxide (dry volume %)	18.6	18.6	18.7	18.7	18.6	18.6
B <sub>w</sub>	Actual water vapor in gas (% by volume) <sup>1</sup>	14.3	14.3	14.3	15.2	15.2	15.2
<b>Gas Flow Rate<sup>2</sup></b>							
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	201,000	205,000	199,000	202,000	204,000	204,000
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	134,000	136,000	132,000	134,000	135,000	136,000
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	115,000	117,000	113,000	114,000	115,000	115,000
<b>Nitrogen Oxides Results</b>							
C <sub>sd</sub>	Concentration (ppmdv)	6.6	6.5	6.6	6.7	6.6	6.6
C <sub>sd-x</sub>	Concentration @ 0% O <sub>2</sub> (ppmdv)	7.7	7.7	7.7	7.8	7.7	7.8
C <sub>sd</sub>	Concentration (lb/dscf)	7.9E-07	7.8E-07	7.9E-07	7.9E-07	7.8E-07	7.9E-07
E <sub>lb/hr</sub>	Emission Rate (lb/hr)	5.4	5.5	5.3	5.4	5.4	5.5
E <sub>T/yr</sub>	Emission Rate (Ton/yr)	24	24	23	24	24	24
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	0.0083	0.0082	0.0083	0.0084	0.0083	0.0084
<b>Carbon Monoxide Results<sup>3</sup></b>							
C <sub>sd</sub>	Concentration (ppmdv)	<0.48	<0.48	<0.48	<0.48	<0.48	<0.48
C <sub>sd-x</sub>	Concentration @ 0% O <sub>2</sub> (ppmdv)	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56
C <sub>sd</sub>	Concentration (lb/dscf)	<3.5E-08	<3.5E-08	<3.5E-08	<3.5E-08	<3.5E-08	<3.5E-08
E <sub>lb/hr</sub>	Emission Rate (lb/hr)	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
E <sub>T/yr</sub>	Emission Rate (Ton/yr)	<1.1	<1.1	<1.0	<1.0	<1.1	<1.1
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04

<sup>2</sup> Average includes 10 runs.

<sup>1</sup> Moisture data obtained from nearly-concurrent Draft ASTM CCM runs.

<sup>2</sup> Flow data used in lb/hr calculations was obtained from nearly-concurrent Method 2 runs.

<sup>3</sup> For CO, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).

**Table 2-4 (Continued):  
NO<sub>x</sub> and CO Emissions (EPA Method 7E/10)**

Run No.		7	8	9	10	Average (all Runs)
Date (2019)		Mar 7	Mar 7	Mar 7	Mar 7	
Start Time (approx.)		16:14	16:46	17:17	17:57	
Stop Time (approx.)		16:35	17:07	17:38	18:18	
<b>Process Conditions</b>						
P <sub>1</sub>	Hydrogen Production (Mscf/day)	58.7	58.7	58.7	58.7	58.7
P <sub>2</sub>	Aqueous NH <sub>3</sub> feed to SCR (lb/hr)	32.8	32.8	32.8	32.8	32.8
P <sub>3</sub>	SCR Inlet Temperature	628	628	628	628	628
F <sub>d</sub>	Oxygen-based F-factor (dscf/MMBtu)	8,985	8,987	8,989	8,989	9,070
H <sub>i</sub>	Actual heat input (MMBtu/hr)	602	602	602	602	602
Cap	Capacity factor (hours/year)	8,760	8,760	8,760	8,760	8,760
<b>Gas Conditions</b>						
O <sub>2</sub>	Oxygen (dry volume %)	3.3	3.1	3.3	3.1	3.2
CO <sub>2</sub>	Carbon dioxide (dry volume %)	18.7	18.5	18.7	18.6	18.5
B <sub>w</sub>	Actual water vapor in gas (% by volume) <sup>1</sup>	12.8	12.8	12.8	15.2	14.9
<b>Gas Flow Rate<sup>2</sup></b>						
Q <sub>a</sub>	Volumetric flow rate, actual (acfm)	185,000	186,000	183,000	186,000	185,000
Q <sub>s</sub>	Volumetric flow rate, standard (scfm)	122,000	123,000	120,000	123,000	121,000
Q <sub>std</sub>	Volumetric flow rate, dry standard (dscfm)	102,000	103,000	101,000	103,000	102,000
<b>Nitrogen Oxides Results</b>						
C <sub>sd</sub>	Concentration (ppmdv)	6.9	6.7	6.9	6.5	6.6
C <sub>sd-x</sub>	Concentration @ 0% O <sub>2</sub> (ppmdv)	8.1	7.9	8.1	7.7	7.8
C <sub>sd</sub>	Concentration (lb/dscf)	8.2E-07	8.0E-07	8.2E-07	7.8E-07	7.9E-07
E <sub>lb/hr</sub>	Emission Rate (lb/hr)	5.7	5.6	5.7	5.4	5.5
E <sub>T/yr</sub>	Emission Rate (Ton/yr)	25	25	25	23	24
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	0.0087	0.0085	0.0087	0.0082	0.0084
<b>Carbon Monoxide Results<sup>3</sup></b>						
C <sub>sd</sub>	Concentration (ppmdv)	<0.48	<0.48	<0.48	<0.48	<0.48
C <sub>sd-x</sub>	Concentration @ 0% O <sub>2</sub> (ppmdv)	<0.57	<0.56	<0.57	<0.56	<0.56
C <sub>sd</sub>	Concentration (lb/dscf)	<3.5E-08	<3.5E-08	<3.5E-08	<3.5E-08	<3.5E-08
E <sub>lb/hr</sub>	Emission Rate (lb/hr)	<0.24	<0.24	<0.24	<0.24	<0.24
E <sub>T/yr</sub>	Emission Rate (Ton/yr)	<1.1	<1.1	<1.1	<1.0	<1.05
E <sub>Fd</sub>	Emission Rate - F <sub>d</sub> -based (lb/MMBtu)	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04	<3.7E-04

<sup>2</sup>Average includes 10 runs.

080410 154528

<sup>1</sup> Moisture data obtained from nearly-concurrent Method 4 run.

<sup>2</sup> Flow data used in lb/hr calculations was obtained from nearly-concurrent Method 2 runs.

<sup>3</sup> For CO, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).

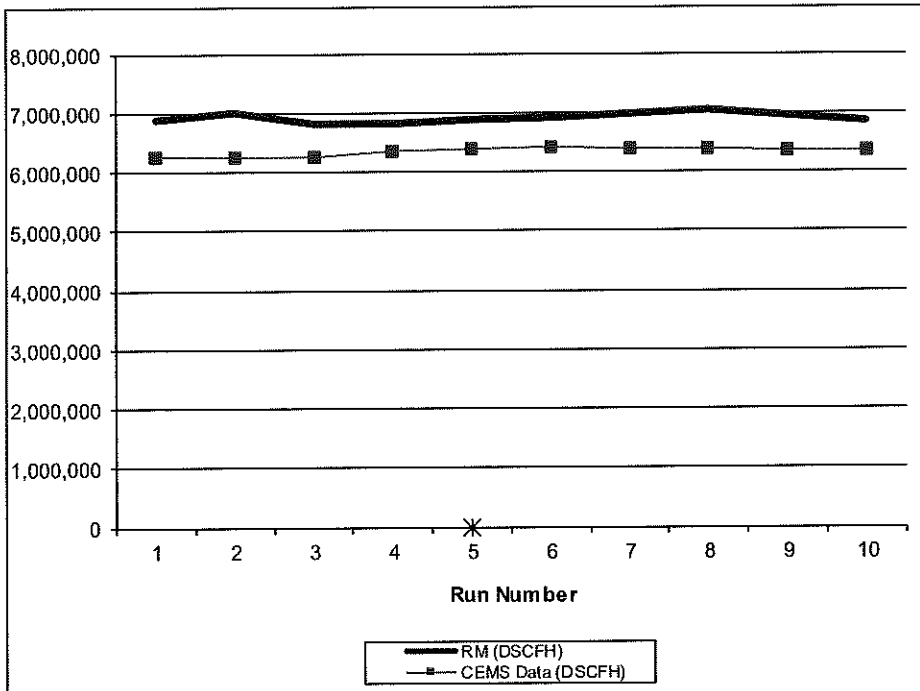
**Table 2-5:  
 Dry Standard Flow Rate RATA (EPA Method 2 / PS 6)**

Run No.	Start Time	Date (2019)	CEMS Data		Difference	
			RM (DSCFH)	(DSCFH)	Difference	Percent
1	09:55	Mar 7	6,893,000	6,262,400	630,600	9.1%
2	10:37	Mar 7	7,007,000	6,260,100	746,900	10.7%
3	11:20	Mar 7	6,807,000	6,270,800	536,200	7.9%
4	11:58	Mar 7	6,824,000	6,342,500	481,500	7.1%
5 *	12:44	Mar 7	6,886,000	6,388,600	497,400	7.2%
6	13:41	Mar 7	6,901,000	6,404,600	496,400	7.2%
7	14:35	Mar 7	6,974,000	6,379,400	594,600	8.5%
8	15:16	Mar 7	7,028,000	6,397,100	630,900	9.0%
9	15:57	Mar 7	6,932,000	6,343,800	588,200	8.5%
10	16:39	Mar 7	6,860,000	6,343,500	516,500	7.5%
<b>Average</b>			<b>6,914,000</b>	<b>6,333,800</b>	<b>580,200</b>	<b>8.4%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	83,613	
Confidence Coefficient (CC)	64,270	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	<b>9.3%</b>	<b>20.0%</b>

RM = Reference Method (CleanAir Data) 032519 092228  
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)  
 RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



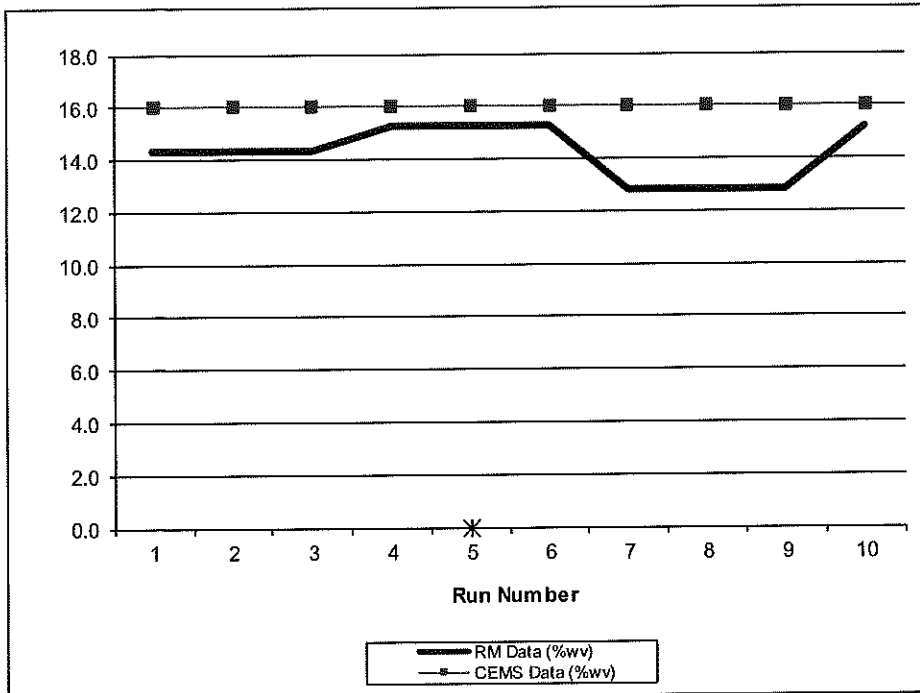
**Table 2-6:  
 H<sub>2</sub>O Concentration RATA (EPA Method 4)**

Run No.	Start Time	Date (2019)	RM Data (%wv)	CEMS Data (%wv)	Difference (%wv)	Difference Percent
1	09:55	Mar 7	14.3	16.0	-1.70	-11.9%
2	10:37	Mar 7	14.3	16.0	-1.70	-11.9%
3	11:20	Mar 7	14.3	16.0	-1.70	-11.9%
4	11:58	Mar 7	15.3	16.0	-0.70	-4.6%
5 *	12:44	Mar 7	15.3	16.0	-0.70	-4.6%
6	13:41	Mar 7	15.3	16.0	-0.70	-4.6%
7	14:35	Mar 7	12.8	16.0	-3.20	-25.0%
8	15:16	Mar 7	12.8	16.0	-3.20	-25.0%
9	15:57	Mar 7	12.8	16.0	-3.20	-25.0%
10	16:39	Mar 7	15.2	16.0	-0.80	-5.3%
<b>Average</b>			<b>14.1</b>	<b>16.0</b>	<b>-1.88</b>	<b>-13.3%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	1.0768	
Confidence Coefficient (CC)	0.8277	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	<b>19.2%</b>	<b>20.0%</b>

RM = Reference Method (CleanAir Data) 032519 092228  
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)  
 RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



**Table 2-7:**  
**O<sub>2</sub> (%dv) RATA (EPA Method 3A / PS 3)**

Run No.	Start Time	Date (2019)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	09:55	Mar 7	3.10	3.10	0.00	0.0%
2	10:37	Mar 7	3.13	3.10	0.03	1.0%
3	11:20	Mar 7	3.10	3.10	0.00	0.0%
4	11:58	Mar 7	3.08	3.10	-0.02	-0.6%
5 *	12:44	Mar 7	3.12	3.10	0.02	0.6%
6	13:41	Mar 7	3.12	3.10	0.02	0.6%
7	14:35	Mar 7	3.28	2.90	0.38	11.6%
8	15:16	Mar 7	3.12	3.10	0.02	0.6%
9	15:57	Mar 7	3.28	3.10	0.18	5.5%
10	16:39	Mar 7	3.09	3.10	-0.01	-0.3%
<b>Average</b>			<b>3.14</b>	<b>3.08</b>	<b>0.07</b>	<b>2.1%</b>

**Relative Accuracy Test Audit Results**

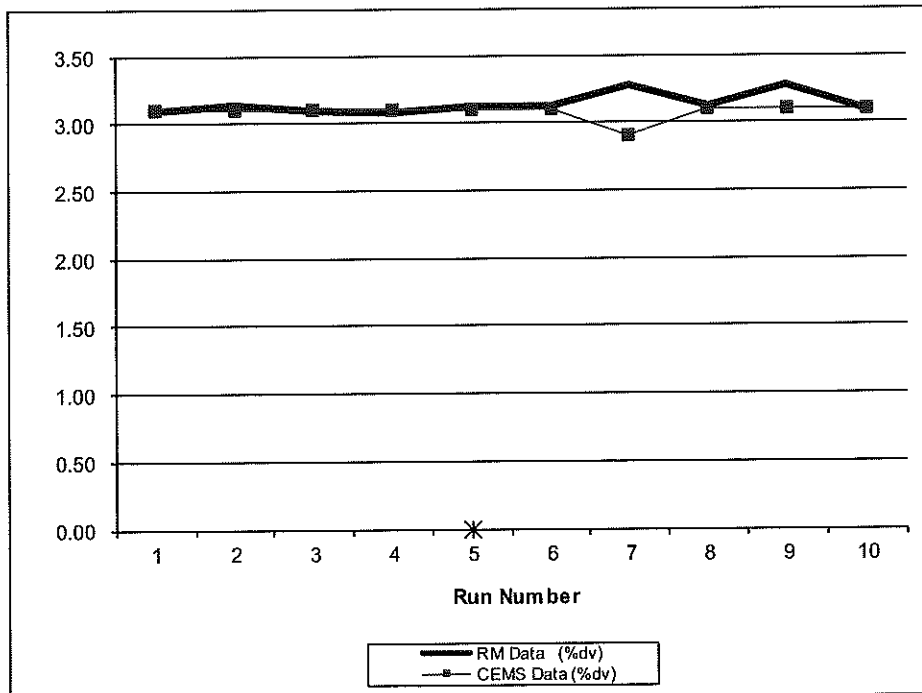
Standard Deviation of Differences	0.1318
Confidence Coefficient (CC)	0.1013
t-Value for 9 Data Sets	2.306
<b>Avg. Abs. Diff. (%dv)</b>	<b>0.07</b>
	<b>Limit</b>
	<b>1.0</b>

RM = Reference Method (CleanAir Data)

032519 092228

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



**Table 2-8:  
 NO<sub>x</sub> (ppmdv) Concentration RATA (EPA Method 7E / PS 2)**

Run No.	Start Time	Date (2019)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1	09:55	Mar 7	6.58	6.00	0.58	8.8%
2	10:37	Mar 7	6.53	5.90	0.63	9.6%
3	11:20	Mar 7	6.58	6.00	0.58	8.8%
4	11:58	Mar 7	6.65	6.00	0.65	9.8%
5 *	12:44	Mar 7	6.57	5.90	0.67	10.2%
6	13:41	Mar 7	6.63	6.00	0.63	9.5%
7	14:35	Mar 7	6.85	6.20	0.65	9.5%
8	15:16	Mar 7	6.71	6.10	0.61	9.1%
9	15:57	Mar 7	6.85	5.80	1.05	15.3%
10	16:39	Mar 7	6.55	6.00	0.55	8.4%
<b>Average</b>			<b>6.66</b>	<b>6.00</b>	<b>0.66</b>	<b>9.9%</b>

**Relative Accuracy Test Audit Results**

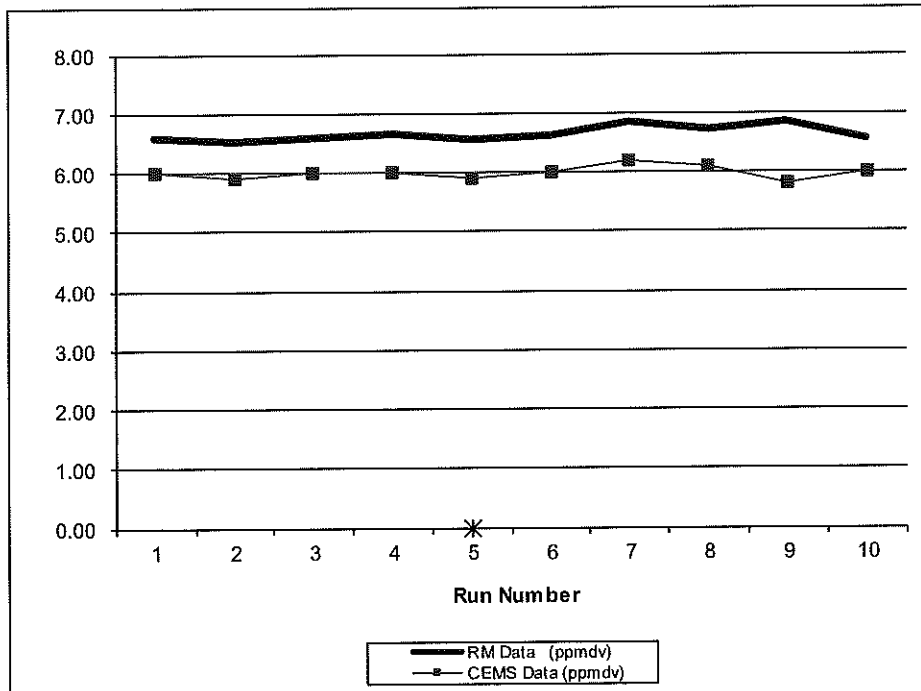
Standard Deviation of Differences	0.1506	
Confidence Coefficient (CC)	0.1158	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	<b>11.6%</b>	<b>20.0%</b>

RM = Reference Method (CleanAir Data)

032519 092228

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



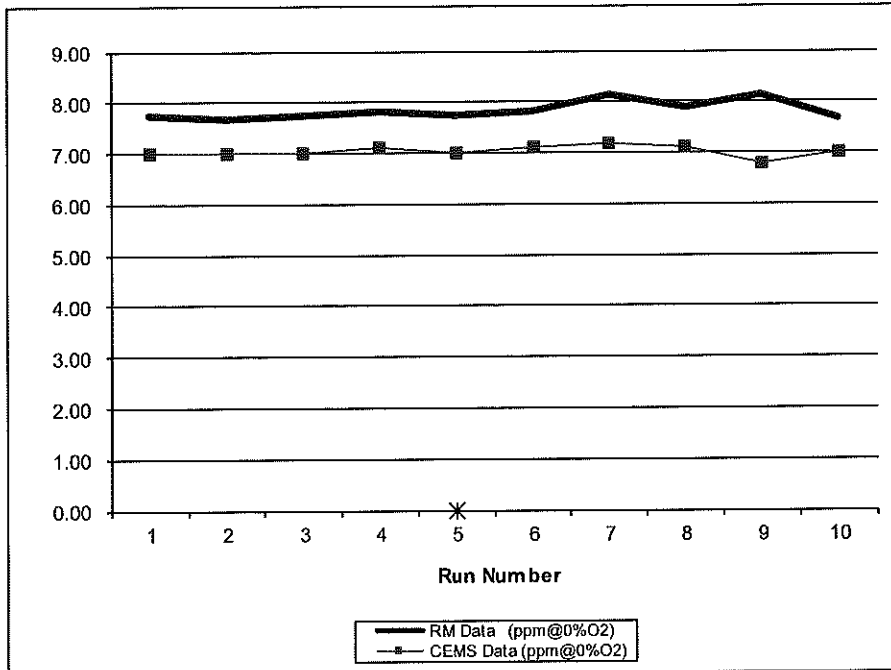
**Table 2-9:  
 NO<sub>x</sub> (ppmdv @ 0% O<sub>2</sub>) Concentration RATA (EPA Method 7E / PS 2)**

Run No.	Start Time	Date (2019)	RM Data (ppm@0%O2)	CEMS Data (ppm@0%O2)	Difference (ppm@0%O2)	Difference Percent
1	09:55	Mar 7	7.73	7.00	0.73	9.4%
2	10:37	Mar 7	7.68	7.00	0.68	8.8%
3	11:20	Mar 7	7.73	7.00	0.73	9.4%
4	11:58	Mar 7	7.80	7.10	0.70	9.0%
5 *	12:44	Mar 7	7.72	7.00	0.72	9.4%
6	13:41	Mar 7	7.80	7.10	0.70	8.9%
7	14:35	Mar 7	8.13	7.20	0.93	11.4%
8	15:16	Mar 7	7.88	7.10	0.78	9.9%
9	15:57	Mar 7	8.13	6.80	1.33	16.3%
10	16:39	Mar 7	7.69	7.00	0.69	8.9%
<b>Average</b>			<b>7.84</b>	<b>7.03</b>	<b>0.81</b>	<b>10.3%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	0.2106	
Confidence Coefficient (CC)	0.1619	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	12.3%	20.0%
Relative Accuracy (as % of Appl. Std.)	1.6%	10.0%
Appl. Std. = 60 ppm@0%O2		

RM = Reference Method (CleanAir Data) 032519 092228  
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)  
 RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.





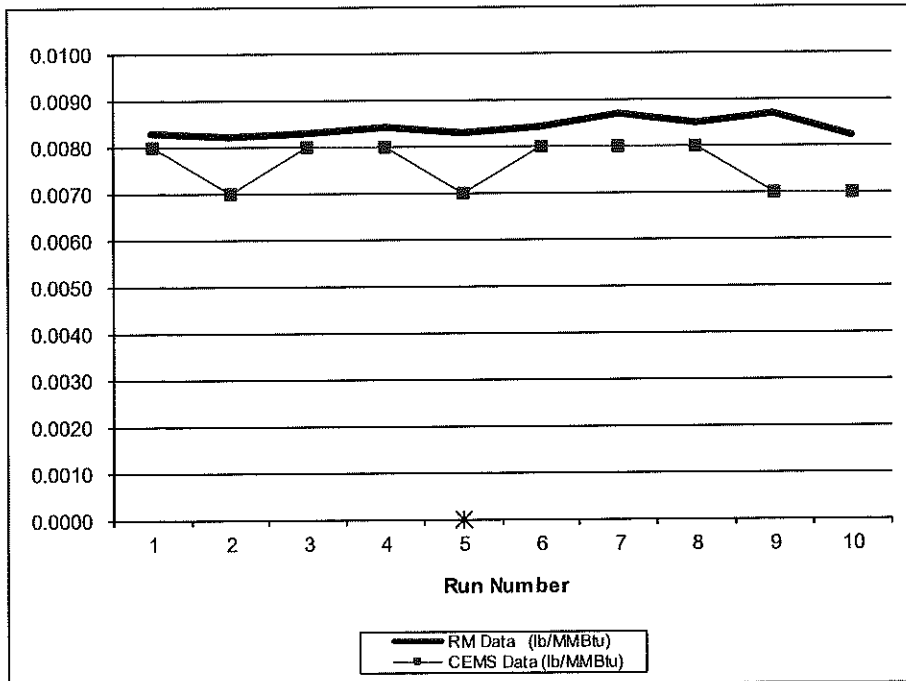
**Table 2-10:**  
**NO<sub>x</sub> (lb/MMBtu) Emission Rate RATA (EPA Method 7E / PS 2)**

Run No.	Start Time	Date (2019)	RM Data (lb/MMBtu)	CEMS Data (lb/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	09:55	Mar 7	0.0083	0.0080	0.0003	3.6%
2	10:37	Mar 7	0.0082	0.0070	0.0012	14.6%
3	11:20	Mar 7	0.0083	0.0080	0.0003	3.6%
4	11:58	Mar 7	0.0084	0.0080	0.0004	4.8%
5 *	12:44	Mar 7	0.0083	0.0070	0.0013	15.7%
6	13:41	Mar 7	0.0084	0.0080	0.0004	4.8%
7	14:35	Mar 7	0.0087	0.0080	0.0007	8.0%
8	15:16	Mar 7	0.0085	0.0080	0.0005	5.9%
9	15:57	Mar 7	0.0087	0.0070	0.0017	19.5%
10	16:39	Mar 7	0.0082	0.0070	0.0012	14.6%
<b>Average</b>			<b>0.0084</b>	<b>0.0077</b>	<b>0.0007</b>	<b>8.9%</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	0.000503	
Confidence Coefficient (CC)	0.000386	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	<b>13.4%</b>	<b>20.0%</b>
Relative Accuracy (as % of Appl. Std.)	<b>8.7%</b>	<b>10.0%</b>
Appl. Std. = 0.013 lb/MMBtu		

RM = Reference Method (CleanAir Data) 032519 092651  
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)  
 RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



**Table 2-11:**  
**CO (ppmdv) Concentration RATA (EPA Method 10 / PS 4A)**

Run No.	Start Time	Date (2019)	RM Data (ppmdv)	CEMS Data (ppmdv)	Difference (ppmdv)	Difference Percent
1	09:55	Mar 7	0.00	0.50	-0.50	NA
2	10:37	Mar 7	0.00	0.50	-0.50	NA
3	11:20	Mar 7	0.00	0.50	-0.50	NA
4	11:58	Mar 7	0.00	0.50	-0.50	NA
5 *	12:44	Mar 7	0.00	0.50	-0.50	NA
6	13:41	Mar 7	0.00	0.50	-0.50	NA
7	14:35	Mar 7	0.00	0.50	-0.50	NA
8	15:16	Mar 7	0.00	0.50	-0.50	NA
9	15:57	Mar 7	0.00	0.50	-0.50	NA
10	16:39	Mar 7	0.00	0.50	-0.50	NA
<b>Average</b>			<b>0.00</b>	<b>0.50</b>	<b>-0.50</b>	<b>NA</b>

**Relative Accuracy Test Audit Results**

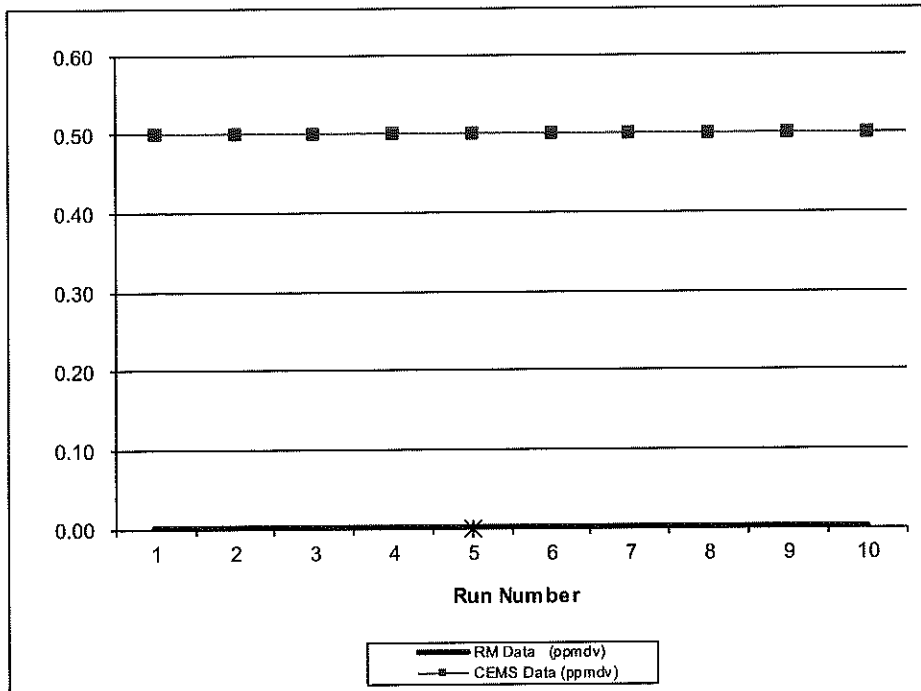
Standard Deviation of Differences	0.0000
Confidence Coefficient (CC)	0.0000
t-Value for 9 Data Sets	2.306
<b>Avg. Abs. Diff. + CC (ppmdv)</b>	<b>0.50</b>
	<b>Limit 5.0</b>

RM = Reference Method (CleanAir Data)

032619 153943

CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)

RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



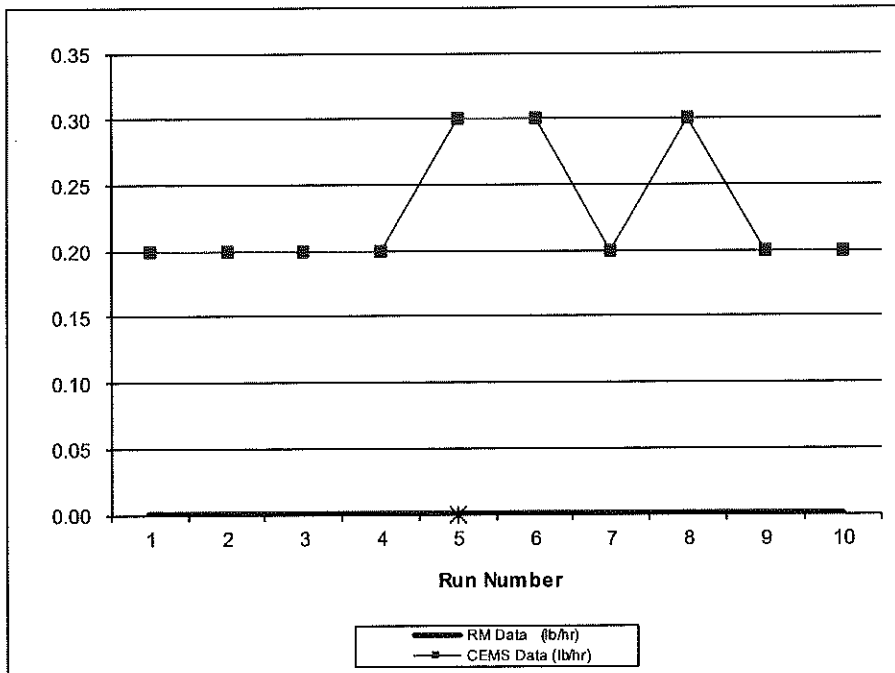
**Table 2-12:**  
**CO (lb/hr) Emission Rate RATA (EPA Method 10 / PS 4A)**

Run No.	Start Time	Date (2019)	RM Data (lb/hr)	CEMS Data (lb/hr)	Difference (lb/hr)	Difference Percent
1	09:55	Mar 7	0.00	0.20	-0.20	NA
2	10:37	Mar 7	0.00	0.20	-0.20	NA
3	11:20	Mar 7	0.00	0.20	-0.20	NA
4	11:58	Mar 7	0.00	0.20	-0.20	NA
5 *	12:44	Mar 7	0.00	0.30	-0.30	NA
6	13:41	Mar 7	0.00	0.30	-0.30	NA
7	14:35	Mar 7	0.00	0.20	-0.20	NA
8	15:16	Mar 7	0.00	0.30	-0.30	NA
9	15:57	Mar 7	0.00	0.20	-0.20	NA
10	16:39	Mar 7	0.00	0.20	-0.20	NA
<b>Average</b>			<b>0.00</b>	<b>0.22</b>	<b>-0.22</b>	<b>NA</b>

**Relative Accuracy Test Audit Results**

Standard Deviation of Differences	0.0441	
Confidence Coefficient (CC)	0.0339	
t-Value for 9 Data Sets	2.306	
Relative Accuracy (as % of Appl. Std.)	<b>0.45%</b>	Limit <b>5.0%</b>
Appl. Std. = 56.9 lb/hr		

RM = Reference Method (CleanAir Data) 032619 153943  
 CEMS = Continuous Emissions Monitoring System (Air Products and Chemical, Inc. Data)  
 RATA calculations are based on 9 of 10 runs. \* indicates the excluded run.



### 3. DESCRIPTION OF INSTALLATION

#### Process Description

Air Products owns and operates the Detroit Hydrogen Plant located within the Marathon Petroleum Company Detroit Refinery. The Hydrogen Plant supplies hydrogen (H<sub>2</sub>) to the Detroit Refinery, which is utilized in the petroleum refining process. Natural gas, refinery fuel gas and/or a high-pentane (C<sub>5</sub>H<sub>12</sub>) refinery stream are converted into 99.9% pure H<sub>2</sub> and high-pressure steam through the use of steam/methane reforming technology. The unit consists of process vessels, a heater, compressors, pumps, piping, drains and other various components (pump and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Hydrogen Plant Heater (EG71-H2HTR) is fired by a combination of refinery gas, pressure swing absorption gas, syngas and/or natural gas. The heater is equipped with a selective catalytic reduction (SCR) system to control emissions, which are vented to the atmosphere via the Hydrogen Plant Heater Stack (SV71-H1).

The testing described in this document was performed at the Hydrogen Plant Heater Stack.

#### Test Location

EPA Method 1 and PS 2 determined the sample point location. Table 3-1 presents the sampling information for the test location. The figures shown on pages 21 and 22 represent the layout of the test location.

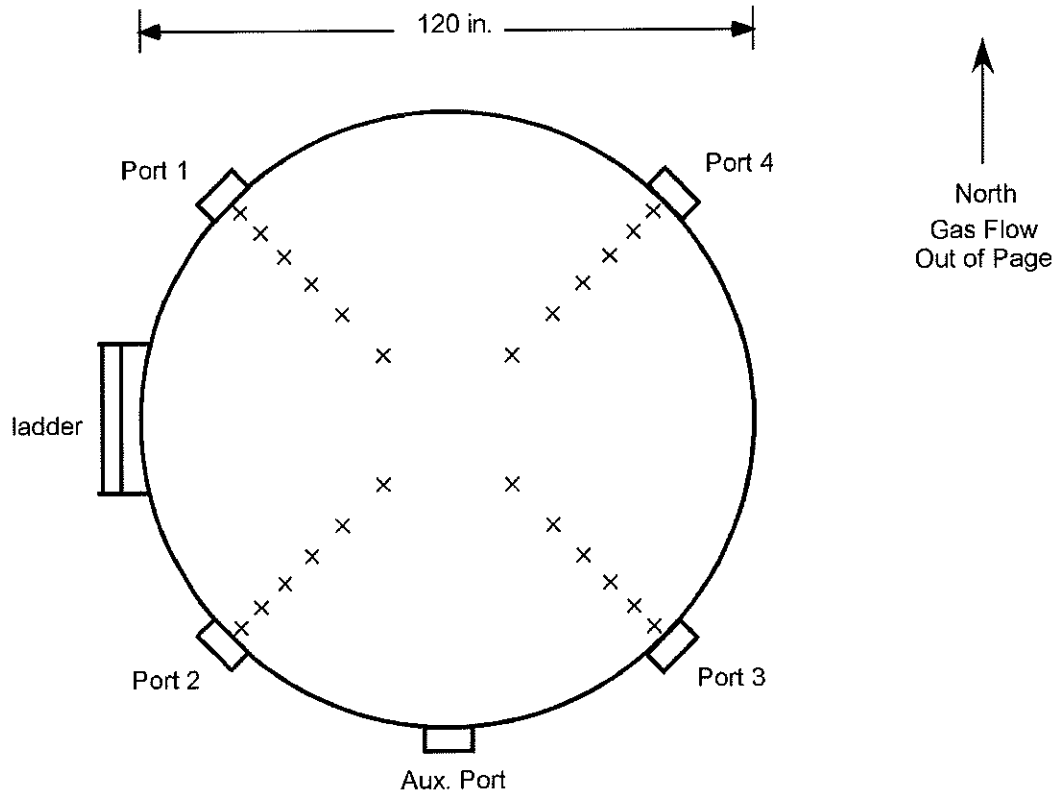
**Table 3-1:  
Sampling Information**

Source Constituent	Method (USEPA)	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<u>H<sub>2</sub> Plant Heater Stack</u>							
Velocity & Flow Rate	M-2	1-10	4	6	varied	varied	3-1
FPM / CPM	M-5/202	1-3	4	6	5	120	3-1
H <sub>2</sub> SO <sub>4</sub>	Mod. CTM-013	1-3	1	1	60	60	N/A <sup>1</sup>
O <sub>2</sub> / CO <sub>2</sub> / THC	M-3A / 25A	1-3	1	1	60	60	3-2 <sup>2</sup>
O <sub>2</sub> / NO <sub>x</sub> / CO (RATAs)	M-3A+PS3 / 7E+PS2 / 10+PS4A	1-10	1	3	7	21	3-2

<sup>1</sup> Sampling occurred at a single point at least 3.3 feet from the duct wall in a port on a lower test plane.

<sup>2</sup> Sampling occurred at a single point at least 3.3 feet from the duct wall.

**Figure 3-1:  
 H<sub>2</sub> Plant Heater Stack, EPA Method 5/202 Sample Point Layout (EPA Method 1)**

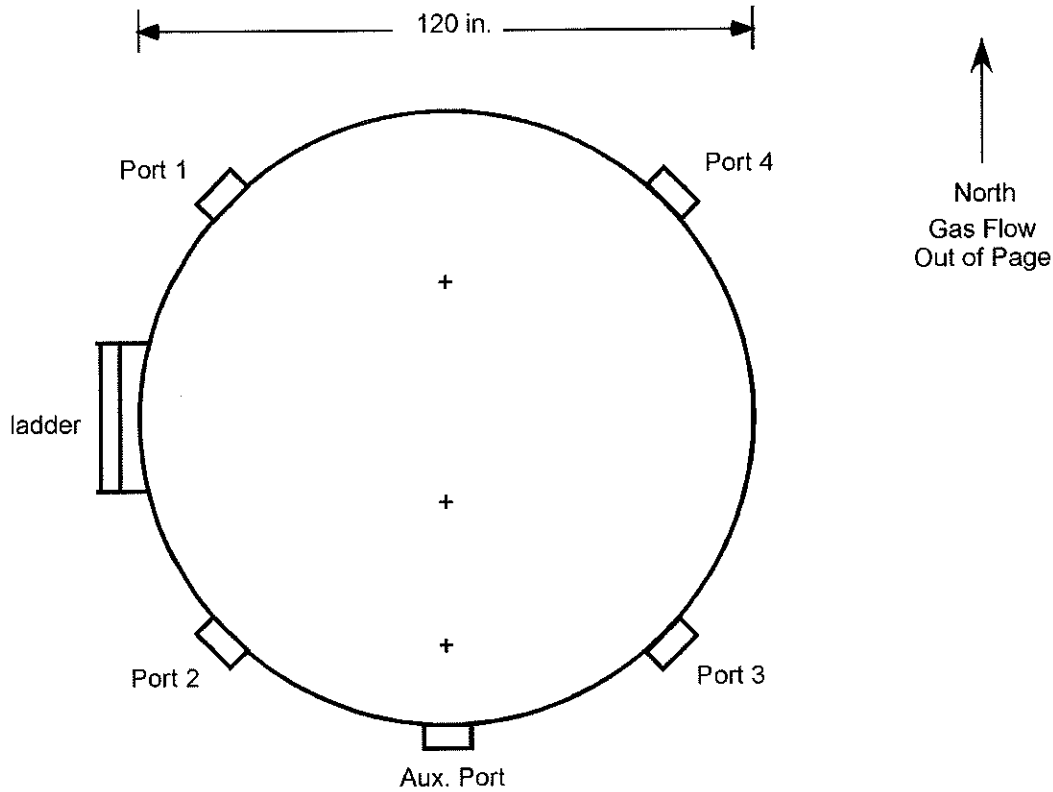


Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	35.6	42.7
2	25.0	30.0
3	17.7	21.2
4	11.8	14.2
5	6.7	8.0
6	2.1	2.5

Duct diameters upstream from flow disturbance (A): 1.9  
 Duct diameters downstream from flow disturbance (B): 5.9

Limit: 0.5  
 Limit: 2.0

**Figure 3-2:  
 H<sub>2</sub> Plant Heater Stack, RATA Sample Point Layout (EPA PS 2)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1		15.7
2		47.2
3		78.7

Duct diameters upstream from flow disturbance (A): 1.9  
 Duct diameters downstream from flow disturbance (B): 5.9

Limit: 0.5  
 Limit: 2.0

## 4. METHODOLOGY

### Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (USEPA) and the Michigan Department of Environmental Quality (DEQ). These methods appear in detail in Title 40 of the CFR and at <https://www.epa.gov/emc>.

Appendix A includes diagrams of the sampling apparatus, as well as specifications for sampling, recovery, and analytical procedures. Any modifications to standard test methods are explicitly indicated in this appendix. In accordance with ASTM D7036 requirements, CleanAir included a description of any such modifications along with the full context of the objectives and requirements of the test program in the test protocol submitted prior to the measurement portion of this project. Modifications to standard methods are not covered by the ISO 17025 and TNI portions of CleanAir's A2LA accreditation.

CleanAir follows specific QA/QC procedures outlined in the individual methods and in USEPA "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source-Specific Methods," EPA/600/R-94/038C. Appendix D contains additional QA/QC measures, as outlined in CleanAir's internal Quality Manual.

#### Title 40 CFR Part 60, Appendix A

Method 1	"Sample and Velocity Traverses for Stationary Sources"
Method 2	"Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)"
Method 3	"Gas Analysis for the Determination of Dry Molecular Weight"
Method 3A	"Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 4	"Determination of Moisture Content in Stack Gases"
Method 5	"Determination of Particulate Matter Emissions from Stationary Sources"
Method 7E	"Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 10	"Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 19	"Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide and Nitrogen Oxide Emission Rates"
Method 25A	"Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"

#### Title 40 CFR Part 60, Appendix B Performance Specifications

PS 2	"Specifications and Test Procedures for SO <sub>2</sub> and NO <sub>x</sub> Continuous Emission Monitoring Systems in Stationary Sources"
PS 3	"Specifications and Test Procedures for O <sub>2</sub> and CO <sub>2</sub> Continuous Emission Monitoring Systems in Stationary Sources"
PS 4A	"Specifications and Test Procedures for Carbon Monoxide Continuous Emission Monitoring Systems in Stationary Sources"

PS 6 "Specifications and Test Procedures for Continuous Emission Rate Monitoring Systems in Stationary Sources"

Title 40 CFR Part 51, Appendix M

Method 202 "Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources"

CTM-013 (Modified)

"Determination of Sulfuric Acid Vapor or Mist and Sulfur Dioxide Emissions from Kraft Recovery Furnaces"

## Methodology Discussion

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### PM and PM<sub>10</sub> Testing – USEPA Method 5/202

PM and PM<sub>10</sub> emissions were determined using EPA Method 5/202. For this test program, PM is assumed equivalent to FPM. PM<sub>10</sub> is equivalent to the sum of FPM less than 10 micrometers ( $\mu\text{m}$ ) in diameter (FPM<sub>10</sub>) and CPM. The Method 5/202 sample train yields a front-half, FPM result and a back-half, CPM result. Where appropriate, the total PM result (FPM plus CPM) from Method 5/202 can be used as a worst-case estimation of Total PM<sub>10</sub> emissions since Method 5 will collect all FPM present in the flue gas (regardless of particle size). Since the Hydrogen Plant Heater is fired by a combination of refinery gas, pressure swing absorption gas, syngas and/or natural gas, the worst-case assumption can safely be made that any FPM in the flue gas exists as FPM<sub>10</sub> and can be collected using standard front-half filtration methods without additional 10  $\mu\text{m}$  speciation.

The front-half (Method 5) of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to 250°F, and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

The back-half (Method 202) of the sampling train is designed to mimic ambient conditions and collect only the particles that would truly form CPM in the atmosphere. It minimizes the sulfur dioxide (SO<sub>2</sub>) and NO<sub>x</sub> interferences observed with earlier versions of the method, in which flue gas was bubbled through cold water and SO<sub>2</sub> and NO<sub>x</sub> were absorbed and partially oxidized before they could be purged out with nitrogen (N<sub>2</sub>).

Flue gas exiting the front-half heated filter passed through a coiled condenser and dry impinger system jacketed by water continually circulated at ambient temperature. Moisture was removed from the flue gas without bubbling through the condensed water. Flue gas then passed through a tetrafluoroethane (TFE) membrane filter at ambient temperature. The temperature of the flue gas at the exit of the filter was directly measured with an in-line thermocouple and maintained in the temperature range of 65°F to 85°F.

After exiting the ambient filter, the flue gas passed through two additional impingers surrounded by ice in a "cold" section of the impinger bucket. The moisture collected in these impingers was not analyzed for CPM and was only collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.



The front-half portion of the sample train (nozzle, probe and heated filter) was recovered per Method 5 requirements, using acetone as the recovery solvent. The back-half of the sample train (heated filter outlet, condenser, dry impingers and TFE membrane filter) was recovered per Method 202 requirements. The impinger train was purged with N<sub>2</sub> at a rate of 14 liters per minute (lpm) for one hour following each test run and prior to recovery.

A field train blank was assembled, purged and recovered as if it were an actual test sample; analysis of the field train blank was used to blank-correct the test run results. Reagent blanks were also collected to quantify background contamination. All samples and blanks were returned to CleanAir Analytical Services for gravimetric analysis. Method 202 samples were maintained at a temperature < 85°F during transport to the laboratory.

## H<sub>2</sub>SO<sub>4</sub> Testing – Modified Conditional Test Method 013 (EPA Method 8A)

H<sub>2</sub>SO<sub>4</sub> emissions are determined referencing CTM-013.

A gas sample was extracted from the source at a constant flow rate from the source using a quartz-lined probe maintained at a temperature of greater than 350°F and a quartz fiber filter maintained at a temperature of greater than 500°F to remove particulate matter.

The sample passed through a H<sub>2</sub>SO<sub>4</sub> condenser, which consisted of a Modified Graham condenser with a type C glass frit, for collection of sulfuric acid vapor and/or mist. The condenser temperature was modified to be maintained at 140°F ± 9°F plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point, which eliminates the oxidation of dissolved SO<sub>2</sub> into the H<sub>2</sub>SO<sub>4</sub>-collecting fraction of the sample train).

After exiting the condenser, the sample gas continued through a series of four (4) glass knock-out jars; two (2) containing water, one (1) empty and one (1) containing silica gel for residual moisture removal. The exit temperature from the knock-out jar set was maintained below 68°F. The sample gas then flowed into a dry gas meter where the collected sample gas volume was determined by means of a calibrated, dry gas meter or an orifice-based flow meter.

The H<sub>2</sub>SO<sub>4</sub>-collecting portion of the sample train was recovered into a single fraction using DI H<sub>2</sub>O as the recovery/extraction solvent; any H<sub>2</sub>SO<sub>4</sub> dissociates into sulfate ion (SO<sub>4</sub><sup>2-</sup>) and is stabilized in the H<sub>2</sub>O matrix until analysis.

Three (3) official 60-minute Modified CTM-013 test runs were performed. H<sub>2</sub>SO<sub>4</sub> emission results have been calculated in units of lb/MMBtu. The final result presented in Table 1-1 is expressed as the average of three (3) valid runs.

Reagent blanks were collected and analyzed to quantify background contamination.

Samples and blanks were returned to CleanAir Analytical Services for ion chromatography (IC) analysis.

## O<sub>2</sub>, CO<sub>2</sub>, and VOC Testing – USEPA Methods 3A and 25A

O<sub>2</sub> and CO<sub>2</sub> concentrations were determined using a paramagnetic / NDIR analyzer per EPA Method 3A. VOC emissions were determined using EPA Method 25A to quantify THC emissions.

The Method 3A/18/25A sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was extracted at a constant rate and delivered at 250°F to a tee at the end of the heated sample line:

- One leg of the tee was connected to a flame ionization analyzer (FIA), which continuously measured minute-average THC concentration expressed in terms of propane ( $C_3H_8$ ) on an actual (wet) basis.
- The other leg of the tee was connected to a gas conditioner, which removed moisture before delivering the gas to a flow panel, and the  $O_2/CO_2$  analyzers, which measured concentration on a dry basis (units of %dv or ppm<sub>dv</sub>).
- No Method 18 gas sample was collected due to the THC concentrations for all three runs being below the analyzer's detection limit of 1% of scale.

The THC analyzer calibration was performed by introducing zero air, high, mid- and low range  $C_3H_8$  calibration gases to the inlet of the sampling system's heated filter. Bias checks were performed before and after each sampling run in a similar manner.

$O_2/CO_2$  calibration error checks were performed by introducing zero  $N_2$ , high range and mid-range calibration gases to the inlet of each analyzer. Bias checks were performed before and after each sampling run by introducing calibration gas to the inlet of the sampling system's heated filter. Per Method 3A, the average results for each run were drift-corrected.

## Flow Rate, Moisture, $O_2$ , $CO_2$ , and $NO_x$ – USEPA Methods 2, 3A, 4, 7E, and 10; PS 2, 3, 4A, and 6

RM flow rate measurements and RA were determined from Type-S Pitot tube traverses per EPA Method 2 and PS 6. RM  $O_2$  and  $CO_2$  emissions and RA were determined using a paramagnetic/NDIR analyzer per EPA Method 3A and PS 3. RM  $NO_x$  emissions and RA were determined using a chemiluminescent analyzer per EPA Method 7E and PS 2. RM CO emissions and RA were determined using an infrared analyzer per EPA Method 10 and PS 4 and/or PS 4A.

The Method 3A/7E/10 sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was extracted at a constant rate at the points specified by the performance specification and delivered at 250°F to a gas conditioner which removed moisture. The flue gas was then delivered via a flow panel to an analyzer bank. Each analyzer measured concentration on a dry basis (units of %dv or ppm<sub>dv</sub>).

Calibration error checks were performed by introducing zero  $N_2$ , high range and mid-range calibration gases to the inlet of each analyzer. Bias checks were performed before and after each sampling run by introducing calibration gas to the inlet of the sampling system's heated filter. Per Method 3A, 7E and 10, the average results for each run were drift-corrected. Documentation of interference checks and  $NO_2$  converter efficiency checks are included in Appendix D of this report.

## General Considerations

A verification of the absence of cyclonic flow was performed at the Hydrogen Plant Heater Stack on March 6, following Method 1 specifications. Documentation is included in Appendix E of this report.

$O_2$  and  $CO_2$  data for the non-instrumental (wet) sampling methods (used in molecular weight calculations and calculation of  $F_i$ -based emissions) was obtained using concurrently-operated Method 3A sampling.

H<sub>2</sub>O data used for moisture correction of concentration data was obtained (when required) in the following manner during the test program:

- For Method 5/202, Method 4 measurements are incorporated into the sampling and recovery procedures.
- For Modified CTM-013, a modified Method 4 measurement is incorporated into the sampling and recovery procedures.
  - Sample gas was extracted through a heated probe at a single point at least one meter from the stack wall. Moisture stratification is not expected at test locations without free water droplets present in the flue gas.
  - Sample gas was extracted at a constant rate no greater than 0.75 cfm and at least 21 scf of flue gas was sampled.
  - After passing through the SAM condenser and filter, the sample gas was drawn through gum rubber tubing and into four iced knock-out jars for moisture collection and measurement. The knock-out jars were arranged in a series and contain identical contents as the impinger train prescribed by Method 4, but with gum rubber connections and stainless-steel internal components.
- For Method 25A, H<sub>2</sub>O data was obtained from concurrently-operated Method 5/202 trains.
- For RATA testing, H<sub>2</sub>O data was obtained from concurrently-operated CTM-013 trains, as outlined above, and one EPA Method 4 train which was used for Run 10.

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*End of Section*